

Vibrational effects in the photoionization shape resonance leading to the $C^2\Sigma_g^+$ state of CO_2^+

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The effect of vibrational averaging on the photoionization cross section and photoelectron asymmetry parameter for photoionization of CO_2 leading to the $C^2\Sigma_g^+$ state of CO_2^+ has been studied. We have computed the photoionization continuum wave function in the frozen-core Hartree-Fock approximation using the iterative Schwinger variational method. Averaging over the symmetric stretching mode of CO_2 reduced the peak resonant cross section by about 15%. This is in contrast to the earlier published results using the continuum multiple-scattering method where a much larger reduction in the peak cross section was obtained. A similar difference between these two theoretical methods was seen in their predicted asymmetry parameters. The present results have also been compared to available experimental data.

I. INTRODUCTION

Recently,¹ we have compared the partial photoionization cross section leading to the $C^2\Sigma_g^+[(4\sigma)^{-1}]$ state of CO_2^+ as obtained by the continuum multiple-scattering model² with that given by the direct solution of the scattering equations for the $e\text{-CO}_2^+$ system. In these studies¹ we explicitly solved the scattering equations for the continuum orbital of the ejected electron in the field of the static-exchange potential of the molecular ion. The feature of particular interest in this channel was the narrow shape resonance which was predicted by the continuum multiple-scattering model (CMSM) to have a peak value of 18 Mb at a photon energy of about 37 eV for the nuclei fixed at the ground-state equilibrium geometry. In contrast, the photoionization cross sections obtained from the solution of the $e\text{-CO}_2^+$ static-exchange collision equations show a somewhat broader resonance feature with a peak value of about 7 Mb at a photon energy of 42 eV.¹ Moreover, Swanson *et al.*² found that vibrational averaging of the fixed-nuclei CMSM cross sections resulted in a considerable reduction and broadening of the resonant peak relative to the results obtained at the equilibrium nuclear configuration. Specifically, vibrational averaging reduced the fixed-nuclei cross section from its peak value of 18 Mb at the ground-state equilibrium geometry to a value of 6

Mb. Although photoionization cross sections near a shape resonance can be expected to be sensitive to changes in internuclear separation, we¹ suggested that this dramatic reduction of the cross section at the equilibrium geometry due to vibrational averaging in the region of the resonance was unphysical and an artifact of the CMSM. Since vibrational motion can indeed lead to important effects in molecular photoionization, it is necessary to quantitatively assess the actual magnitude of the effect of vibrational averaging on molecular photoionization in the region of shape resonances.

In this paper we present vibrationally averaged cross sections and asymmetry parameters for photoionization of the $4\sigma_g$ level of CO_2 leading to the $C^2\Sigma_g^+$ state of CO_2^+ . These results are obtained by averaging the fixed-nuclei photoionization cross sections and asymmetry parameters at five values of the internuclear coordinates over the ground vibrational wave function of the symmetric stretching mode of the molecule. At each internuclear geometry the cross sections are obtained from the solution of the $e\text{-CO}_2^+$ collisional equations with the full static-exchange potential of the ion. These results show that vibrational averaging, in fact, reduces the peak intensity of the fixed-nuclei resonant cross section at the ground-state equilibrium geometry by about 15%. These results are in strong contrast to those of the CMSM where vibrational averaging reduced the intensity of the reso-

nance by 70% in this channel.² These results clearly suggest that the CMSM does not provide a quantitatively realistic description of this resonant photoionization cross section and the effects of vibrational averaging on these cross sections.

In the next section we briefly outline our method of solution of the $e\text{-CO}_2^+$ scattering equations. We then present both the fixed-nuclei and vibrationally averaged cross sections and asymmetry parameters. We compare our results with those of the CMSM and experimental results where available.

II. THEORY AND RESULTS

The fixed-nuclei photoionization cross section for going from an initial bound state Ψ_i to the continuum state $\Psi_{f,\vec{k}}$ due to linearly polarized light is given in the dipole length approximation by

$$\frac{d^2\sigma^L(R)}{d\Omega_{\vec{k}}d\Omega_{\hat{n}}} = \frac{4\pi^2}{c} Ek \left| \langle \Psi_i(R) | \vec{r} \cdot \hat{n} | \Psi_{f,\vec{k}}^{(-)}(R) \rangle \right|^2, \quad (1)$$

and in the dipole velocity approximation by

$$\frac{d^2\sigma^V(R)}{d\Omega_{\vec{k}}d\Omega_{\hat{n}}} = \frac{4\pi^2 k}{cE} \left| \langle \Psi_i(R) | \vec{\nabla} \cdot \hat{n} | \Psi_{f,\vec{k}}^{(-)}(R) \rangle \right|^2, \quad (2)$$

where E is the photon energy, \hat{n} is the direction of the polarization of the light, c is the speed of light, and \vec{k} is the asymptotic momentum of the photoelectron. When these cross sections are averaged over all possible molecular orientations in the laboratory frame, the resulting differential cross section is of the form

$$\frac{d\sigma^{L,V}(R)}{d\Omega_{\vec{k}}} = \frac{\sigma^{L,V}(R)}{4\pi} [1 + \beta_{\vec{k}}^{L,V}(R) P_2(\cos\theta)], \quad (3)$$

where θ is the angle between the direction of the polarization of the light and the momentum of the photoelectron.

The adiabatic-nuclei cross section can then be obtained from the fixed-nuclei results by averaging over the vibrational degrees of freedom. If only the ground vibrational state is initially populated and we sum over all final vibrational states then, by ignoring the dependence of k on the vibrational energy levels, we obtain the vibrationally averaged cross sections³

$$\sigma_{\text{av}}^{L,V} = \langle \chi_i | \sigma^{L,V}(R) | \chi_i \rangle, \quad (4)$$

and

$$\beta_{\vec{k},\text{av}}^{L,V} = \frac{\langle \chi_i | \sigma^{L,V}(R) \beta_{\vec{k}}^{L,V}(R) | \chi_i \rangle}{\langle \chi_i | \sigma^{L,V}(R) | \chi_i \rangle}, \quad (5)$$

where χ_i is the ground-state vibrational wave function. In this study we assume that the vibrational motion of CO_2 is harmonic and we have only considered the effects of averaging over the symmetric stretching mode.

We have carried out the vibrational averaging by performing a five-point Gaussian quadrature where the square of the vibrational wave function is the weight function. Thus, with a symmetric stretch vibrational frequency of 1388.17 cm^{-1} for CO_2 ,⁴ we have computed the fixed-nuclei cross sections at $R(\text{C-O}) = 2.0892, 2.1445, 2.1944, 2.2443$, and 2.2996 a.u. The quadrature weights were then $0.011257, 0.222076, 0.533333, 0.222076$, and 0.011257 , respectively.

The initial-state function [Ψ_i of Eqs. (1) and (2)] was represented by a SCF (self-consistent-field) wave function which was constructed from a $(3s\ 2p\ 1d)$ contracted Cartesian Gaussian basis set.⁵ The SCF energy of CO_2 in this basis set is -187.674286 a.u. at the equilibrium $R(\text{C-O}) = 2.1944 \text{ a.u.}$ The final-state wave functions [$\Psi_{f,\vec{k}}$ of Eqs. (1) and (2)] were obtained using the Frozen-Core-Hartree-Fock (FCHF) approximation. This implies that all the bound orbitals were fixed as their initial-state forms. The continuum orbital representing the photoelectron was then determined by solving the appropriate static-exchange Lippmann-Schwinger equation

$$\Psi_{\vec{k}}^{(-)} = \phi_{\vec{k}} + G_c^{(-)}(E) U \psi_{\vec{k}}^{(-)}, \quad (6)$$

where $E = k^2/2$, $G_c^{(-)}(E)$ is the Coulomb Green's function, U is the static-exchange potential with the $1/r$ component removed, and $\phi_{\vec{k}}$ is a Coulomb scattering function. We have solved Eq. (6) using the Schwinger variational method.⁶ We have not employed the iterative technique which has been applied to other systems,^{7,8} since in our previous studies of the photoionization of CO_2 we found that the exact iterative cross section for photoionization leading to the $C^2\Sigma_g^+$ state of CO_2^+ was very close to the initial noniterative result obtained using the L^2 basis functions given in Table I.⁹ Using the Schwinger variational expression the solutions of Eq. (6) are given by^{6,7}

TABLE I. Scattering basis sets used with the Schwinger variational expression.^a

Number of functions ^b	Center	$4\sigma_g \rightarrow k\sigma_u$		Range of exponents
		l	m	
7	O	0	0	32.0-0.5
5	O	1	0	8.0-0.5
3	O	2	0	2.0-0.5
7	C	1	0	32.0-0.5
5	C	3	0	8.0-0.5
3	C	5	0	2.0-0.5
$4\sigma_g \rightarrow k\pi_u$				
6	O	1	1	16.0-0.5
5	O	2	1	8.0-0.5
5	C	1	1	8.0-0.5
5	C	3	1	8.0-0.5

^aThese basis sets are composed of spherical Gaussian functions as defined in Eq. (9) and correspond to the set R of Eq. (7).

^bTotal number of basis functions on a given center with the same value of l and m . The exponents of the basis set form a geometric series with a ratio of 2.0.

$$\psi_{\vec{k}}^{(-)}(\vec{r}) = \phi_{\vec{k}}^{(-)}(\vec{r}) + \sum_{\alpha_i, \alpha_j \in R} \langle \vec{r} | G_c^{(-)} U | \alpha_i \rangle [D^{-1}]_{ij} \times \langle \alpha_j | U | \phi_{\vec{k}} \rangle, \quad (7)$$

where $[D^{-1}]_{ij}$ is the matrix inverse of

$$D_{ij} = \langle \alpha_i | U - U G_c^{(-)} U | \alpha_j \rangle. \quad (8)$$

The sets of functions R used in Eq. (7) are composed of spherical Gaussian functions defined by

$$\alpha^{\gamma, l, m, n, \vec{A}}(\vec{r}) = N |\vec{r} - \vec{A}|^l e^{-\gamma |\vec{r} - \vec{A}|^2} Y_{lm}(\Omega_{\vec{r} - \vec{A}}). \quad (9)$$

In Table I we give the elements of these sets for the two scattering symmetries considered here. The necessary integrals are computed by expanding all functions in truncated partial-wave expansions with the resulting radial integrals put on a grid and computed using Simpson's rule. We have used the same grid and expansion parameters as were used in our earlier study of CO₂ photoionization.⁹ The grid contained 1000 points extending out to $r = 90$ a.u. The smallest step size was 0.005 a.u. and the largest step size was 0.16 a.u. We have expanded the static potential including terms up to $\lambda_m^{\text{dir}} = 118$. In the exchange integrals, the occupied orbitals were expanded to a high enough l such that the orbitals were normalized to better than

0.99, and the expansion of $1/r_{12}$ was truncated at $\lambda_m^{\text{ex}} = 40$. All other partial-wave expansions were truncated at $l_m = 59$.

In Fig. 1 we present the fixed-nuclei photoionization cross sections of CO₂ leading to the $C^2\Sigma_g^+$ state of CO₂⁺ for the five internuclear separations given above. We have taken the vertical ionization potential for the $C^2\Sigma_g^+$ state of CO₂⁺ to be 19.4

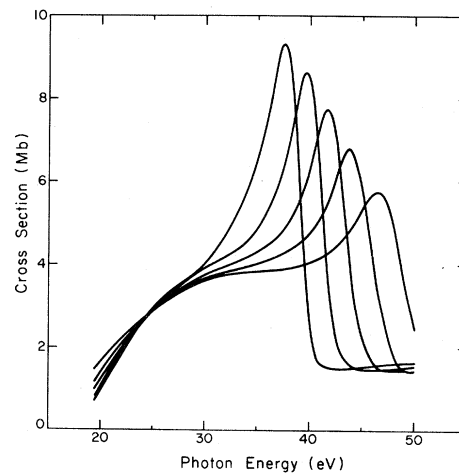


FIG. 1. Fixed-nuclei photoionization cross sections of CO₂ leading to the $C^2\Sigma_g^+$ state of CO₂⁺. The five curves correspond from left to right to $R(\text{C-O}) = 2.2996, 2.2443, 2.1944, 2.1445,$ and 2.0892 a.u. One megabarn (Mb) is 10^{-18} cm^2 .

eV.¹⁰ We can see that the photoionization cross sections depend fairly strongly on R in the region of the shape resonance in this channel. At larger internuclear separations the resonance moves to lower energy, and at shorter internuclear separations to higher energy. In Fig. 2 we compare the present dipole length static-exchange level cross sections, both vibrationally averaged and fixed-nuclei, with those obtained using the CMSM approach,² and with the experimental results of Brion and Tan.¹¹ We can see that the effect of averaging on the static-exchange cross section is to broaden the resonant feature and to reduce the cross section. As can be seen in Fig. 2, the CMSM fixed-nuclei and vibrationally averaged cross sections exhibit the same qualitative trend. However, the CMSM cross sections show a much larger decrease in the peak cross section due to vibrational averaging. The experimental total cross section does not show any obvious resonance feature in this channel.

In this study we have not included the effects of initial- or final-state correlation. One way of estimating such correlation effects is to compute the photoionization cross section in both the dipole length and velocity forms. In Fig. 3 we present the length and velocity forms of the vibrationally averaged cross section leading to the $C^2\Sigma_g^+$ state of CO_2^+ and compare them to the experimental results of Brion and Tan.¹¹ The difference between

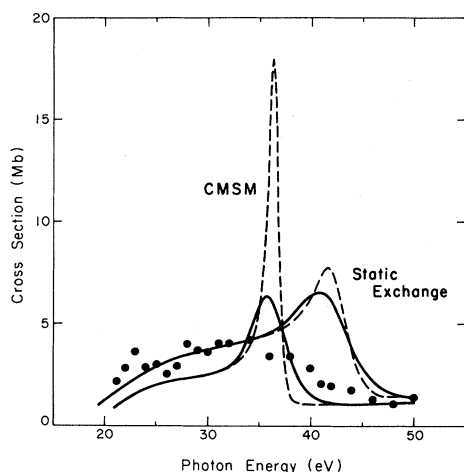


FIG. 2. Comparison of the CMSM results from Ref. 2 and the present static-exchange results for the photoionization cross section of CO_2 leading to the $C^2\Sigma_g^+$ state of CO_2^+ : — cross section averaged over the symmetric stretch vibrational mode; - - - equilibrium fixed-nuclei cross section; ● experimental results of Brion and Tan from Ref. 11.

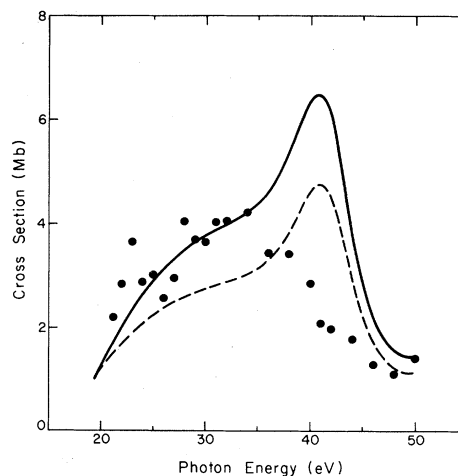


FIG. 3. Vibrationally averaged photoionization cross section leading to the $C^2\Sigma_g^+$ state of CO_2^+ : — dipole length static-exchange cross section; - - - dipole velocity static-exchange cross section; ● experimental results of Brion and Tan from Ref. 11.

the length and velocity cross sections can be viewed as an estimate of the minimum error due to correlation.¹² In actual applications^{8,9,13} we have found that the exact cross sections tend to lie between the length and velocity forms, except where autoionization is important. Some of the disagree-

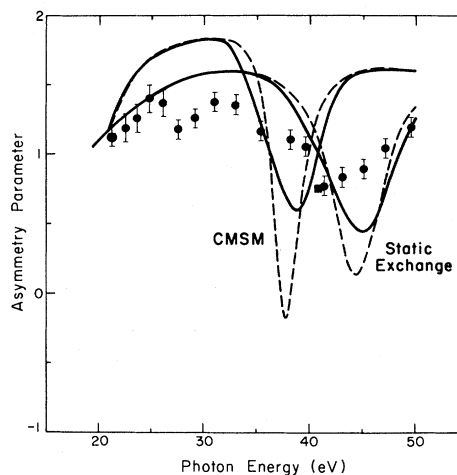


FIG. 4. Comparison of the CMSM results from Ref. 14 and the present static-exchange results for the photoelectron asymmetry parameter for photoionization leading to the $C^2\Sigma_g^+$ state of CO_2^+ : — asymmetry parameter averaged over the symmetric stretch vibrational mode; - - - equilibrium fixed-nuclei asymmetry parameter; ● experimental data of Carlson *et al.* from Ref. 16; ■ experimental data of Katsumata *et al.* from Ref. 15.

ment between theory and experiment shown in Fig. 3 could generally be due to correlation effects. In this system, however, the disagreement could also arise from the neglect of vibrational averaging of the photoionization cross section over the asymmetric stretching and bending modes in the present calculation.

In Fig. 4 we examine the effects of vibrational averaging on the photoelectron asymmetry parameters in the $C^2\Sigma_g^+$ channel. We have compared the static-exchange results obtained here with the CMSM results of Swanson *et al.*¹⁴ and with experimental data of Katsumata *et al.*¹⁵ and Carlson *et al.*¹⁶ Unlike the experimental total photoionization cross sections,¹¹ the experimental asymmetry parameters¹⁶ do show a resonant feature at a photon energy of 40 eV, in reasonable agreement with the present theoretical results. Once again the vibrational averaging of the CMSM results produces a larger quantitative change than does vibrational averaging of the static-exchange results.

III. CONCLUSION

We have shown that vibrational averaging of the static-exchange photoionization cross section of CO_2 leading to the $C^2\Sigma_g^+$ state of CO_2^+ leads to a 15% reduction in the peak resonant cross section. A similar reduction in the feature in the computed photoelectron asymmetry parameters was also ob-

tained. This is in contrast to the larger effects predicted by the CMSM calculations.^{2,14} It is also of interest to note that the resonant vibrational effects obtained here for the photoionization of CO_2 are much larger than those obtained by Raseev *et al.*¹⁷ for the resonant photoionization of N_2 leading to the $X^2\Sigma_g^+$ state of N_2^+ . This seems to follow directly from the fact that the shape resonance in CO_2 is much narrower than that in N_2 .

The present theoretical results do not yet agree quantitatively with the experimental results for the photoionization cross section. However, the experimental asymmetry parameters of Carlson *et al.*¹⁶ lend strong support to the theoretical prediction of a shape resonance occurring in the $C^2\Sigma_g^+$ channel near a photon energy of 40 eV.

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